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On the Leading Energy Correction for the Statistical Model of the Atom: Non-Interacting Case

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It is shown that the infima of the Hellmann and the Hellmann-Weizsäcker functional without electron-electron interaction can be written in terms of the nuclear charge Z and the particle number N as $E(Z,N)=Z^2(\alpha_1 N^{1/3}+\alpha_2+\dots)$. *In the case of Hellmann functional we calculate both* α_1 *and* α_2, *in the case of the Hellmann-Weizsäcker functional we calculate* α_1. *We compare our results with Thomas-Fermi theory. Finally, we apply our result to bound the quantum mechanical ground state energy of the system.*

1. Introduction

We are interested in a system of N electrons moving in the field of a nucleus of charge Z. The Hamiltonian of such a system is

$$(1.1)\qquad H=\sum_{i=1}^{N}\left(-\Delta_i-\frac{Z}{|\mathbf{r}_i|}\right)+\sum_{\substack{i,j=1\\ i<j}}^{N}\frac{1}{|\mathbf{r}_i-\mathbf{r}_j|}.$$

Let $E_Q(Z,N)$, the quantum mechanical ground state energy, be the infimum of the spectrum of H for the self-adjoint realization of H on $\bigwedge_{i=1}^{N}(L^2(\mathbb{R}^3)\otimes\mathbb{C}^q)$, where q is the number of spin states, in our case $q=2$. Several approximation schemes have been developed to solve the associated Schrödinger equation. A review is given by Gombas [1,2]. One of those approximation schemes is the Thomas-Fermi theory (Thomas [3], Fermi [4]). For this model the energy of $N=\lambda Z$ electrons in the field of a nucleus of charge Z is

$$(1.2)\qquad E_Z^{TF}(N)=Z^{7/3}E_1^{TF}(\lambda).$$

Later Lieb and Simon [5] showed that this is just the leading term in the quantum mechanical case, when Z- and hence N-approaches infinity.

But already in 1952 Scott [6] had conjectured that the Thomas-Fermi theory should be corrected by a term of order Z^2. For a neutral atom he proposed

$$(1.3)\qquad E_Q(Z,N=Z)=Z^{7/3}E_1^{TF}(1)+\frac{q}{8}Z^2+o(Z^2).$$

The Z^2-correction has its origin in the electrons near the nucleus, where the electron-nucleus interaction is supposed to dominate the electron-electron interaction. Thus

Scott's formula should be correct regardless of the presence of electron-electron interaction, if $E_1^{TF}(1)$ is understood to be the infimum of the corresponding Thomas-Fermi functional with or without interaction, respectively. But this is still an open question. Our purpose in the present paper is to do one step on the way proving this conjecture.

One of the authors [7] showed that the Hellmann-Weizsäcker functional is an upper bound of $E_Q(Z,N)$, if N_ℓ, the number of electrons in the angular momentum channel ℓ, is an integer multiple of $q(2\ell+1)$ for every ℓ. In a previous paper [8] we examined various properties of the Hellmann and the Hellmann-Weizsäcker functional with and without interaction and gave a generalization of the upper bound of [7] allowing for arbitrary values for N_ℓ. Since the Z^2-correction should be independent of the electron-electron interaction we consider the Hellmann and the Hellmann-Weizsäcker functional of N non-interacting electrons. The aim of this paper is to show that the Hellmann-Weizsäcker functional provides a Z^2-correction of the Thomas-Fermi model and furthermore because [7] and [8] can be used to bound $E_Q(Z,N)$. As a corollary we obtain

$$E_Q(Z,N=Z) \leq E_1^{TF}(1)Z^{7/3} + O(Z^2), \tag{1.4}$$

a well known result for the Bohr atom. However, our method of proving (1.4) is not restricted to this case, but generalizes to the interacting one [9].

In chapter two we give the asymptotic behavior of the infimum of the Hellmann functional, i.e. the functional without gradient term. In the third chapter we show that the presence of the gradient term changes the energy only of order Z^2. This will give us the proposed result, which is stated in chapter four. In a subsequent paper we shall come back to this very point for the case, where interaction is taken into account as well.

2. Infimum of the Hellmann Functional

We define the Hellmann energy functional to be

$$\tilde{\mathcal{E}}_Z^H(\underline{\rho}) = \sum_{\ell=0}^{\infty} \mathcal{E}_{\ell,Z}^H(\rho_\ell) \tag{2.1}$$

with

$$\mathcal{E}_{\ell,Z}^H(\rho_\ell) = \int_0^\infty \left(\frac{1}{3}\alpha_\ell\rho_\ell^3(r) + \left(\frac{\beta_\ell}{r^2} - \frac{Z}{r}\right)\rho_\ell(r)\right) dr. \tag{2.2}$$

$\mathcal{E}_{\ell,Z}^H$, and $\tilde{\mathcal{E}}_Z^H$ are defined on the function sets

$$\begin{aligned} G &= \{\rho|\rho \geq 0,\ \rho\epsilon L^1(\mathbb{R}^+) \cap L^3(\mathbb{R}^+),\ \frac{\rho}{r^2}\epsilon L^1(\mathbb{R}^+)\} \text{ and} \\ M &= \{\underline{\rho}\epsilon L^3(\mathbb{R}^+ \times \mathbb{N}_0, d\mu)|\underline{\rho} \geq 0,\ \sum_{\ell=0}^\infty \beta_\ell \int_0^\infty \frac{\rho_\ell}{r^2}dr < \infty,\ \sum_{\ell=0}^\infty \int_0^\infty \rho_\ell dr < \infty\}, \end{aligned} \tag{2.3}$$

respectively, where $\underline{\varrho}$ stands for $(\varrho_0, \ldots, \varrho_\ell, \ldots)$, and $d\mu$ is the Lebesgue measure in the first and the counting measure weighted by α_ℓ in the second co-ordinate. In order to establish contact with quantum theory let us choose

$$(2.4) \qquad \alpha_\ell = \left(\frac{\pi}{q(2\ell+1)}\right)^2, \qquad \beta_\ell = (\ell + \frac{1}{2})^2.$$

First we calculate the ground state energy of $\tilde{\mathcal{E}}_Z^H$ under the condition

$$(2.5) \qquad N = \sum_{\ell=0}^{\infty} N_\ell, \qquad N_\ell = \int_0^\infty \rho_\ell dr.$$

Therefore we consider the Euler-Lagrange equation of the functional

$$(2.6) \qquad \mathcal{E}_{\ell,Z}^H(\rho_\ell) = \int_0^\infty \left(\frac{1}{3}\alpha_\ell \rho_\ell^3(r) + (\frac{\beta_\ell}{r^2} - \frac{Z}{r} - \lambda)\rho_\ell(r)\right) dr + \lambda N_\ell,$$

which is

$$(2.7) \qquad \rho_\ell(r) = \frac{q(2\ell+1)}{\pi r}\sqrt{\left[-(\ell+\frac{1}{2})^2 + Zr + \lambda r^2\right]_+} \quad .$$

The norm condition (2.5) determines the Lagrange multiplier λ as follows

$$(2.8) \qquad \lambda = -Z^2\left(\frac{q(2\ell+1)}{2N_\ell + q(2\ell+1)^2}\right)^2.$$

Inserting (2.7) and (2.8) into the functional and carrying out the integration yields

$$(2.9) \qquad E_{\ell,Z}^H(N_\ell) = \inf_{\rho_\ell \in G} \mathcal{E}_{\ell,Z}^H(\rho_\ell) = -Z^2 \frac{qN_\ell}{2N_\ell + q(2\ell+1)^2}.$$

Next we determine the quantities N_ℓ in order to minimize $\tilde{\mathcal{E}}_Z^H$ under the condition $N = \sum_\ell N_\ell$. So we look for minima of

$$(2.10) \qquad \tilde{\mathcal{E}}_Z^H = \sum_\ell \left(-Z^2 \frac{qN_\ell}{2N_\ell + q(2\ell+1)^2} - \mu N_\ell\right) + \mu N.$$

Necessary conditions for a stationary point are

$$(2.11) \qquad \frac{\partial \tilde{\mathcal{E}}_Z^H}{\partial N_\ell} = -Z^2\left(\frac{q(2\ell+1)}{2N_\ell + q(2\ell+1)^2}\right)^2 - \mu = 0, \quad (\ell = 0, 1, 2, \ldots).$$

This yields

$$(2.12) \qquad N_\ell = q(2\ell+1)\left[\frac{Z}{2\sqrt{-\mu}} - \frac{1}{2} - \ell\right]_+ = q(2\ell+1)[k-\ell]_+,$$

where we defined $k = \frac{Z}{2\sqrt{-\mu}} - \frac{1}{2}$. The sum in (2.10) runs over those ℓ, which are less than k, since $N_\ell > 0$. We define k' to be the greatest integer less than k and $\varepsilon = k - k'$. So

$0<\varepsilon\leq 1$. One will find just these occupation numbers, if one assumes k' shells to be filled completely, while the $(k'+1)^{st}$ shell is filled by a fraction ε.

Inserting (2.12) into (2.10) and carrying out the sum yields

$$(2.13)\quad \tilde{E}_Z^H = \inf \tilde{\mathcal{E}}_Z^H = -\frac{Z^2 q}{2k+1}\sum_{\ell=0}^{k'}(k-\ell) = -\frac{Z^2 q}{2k+1}\left(k(k'+1)-\frac{1}{2}k'(k'+1)\right).$$

The condition $\sum\limits_{\ell=0}^{k'} q(2\ell+1)(k-\ell) = N$ determines k and hence k' and ε. One finds

$$(2.14)\quad N = q\left(\frac{k'^3}{3}+\frac{k'^2}{2}+\frac{k'}{6}\right)+\varepsilon q(k'+1)^2.$$

This yields

$$(2.15)\quad \begin{aligned} k' &= \left(\frac{3}{q}\right)^{1/3}N^{1/3}-\frac{1}{2}-\varepsilon+O(N^{-1/3}),\\ k &= \left(\frac{3}{q}\right)^{1/3}N^{1/3}-\frac{1}{2}+O(N^{-1/3}). \end{aligned}$$

Inserting (2.15) into (2.13) we obtain

THEOREM 1.

$$\tilde{E}_Z^H(N) = -\frac{Z^2 q}{4}\left(\frac{3}{q}\right)^{1/3}N^{1/3}+Z^2 O(N^{-1/3}).$$

We remark that $-\frac{Z^2 q}{4}\left(\frac{3}{q}\right)^{1/3}N^{1/3}$ is just equal to $\tilde{E}_Z^{TF}(N)$, the infimum of the Thomas-Fermi functional in the noninteracting case.

3. Infimum of the Hellmann-Weizsäcker Functional

The Hellmann-Weizsäcker functional is

$$(3.1)\quad \tilde{\mathcal{E}}_Z^{HW}(\underline{\rho}) = \sum_{\ell=0}^{\infty}\mathcal{E}_{\ell,Z}^{HW}(\rho_\ell),$$

where

$$(3.2)\quad \mathcal{E}_{\ell,Z}^{HW}(\rho_\ell) = \int_0^\infty \left(\sqrt{\rho_\ell}'^2+\frac{\pi^2}{3q^2(2\ell+1)^2}\rho_\ell^3+\left(\frac{\ell(\ell+1)}{r^2}-\frac{Z}{r}\right)\rho_\ell\right)dr.$$

Each $\mathcal{E}_{\ell,Z}^{HW}$ is defined on the function space F, while $\tilde{\mathcal{E}}_Z^{HW}$ is defined on W:

$$(3.3)\quad \begin{aligned} F &= \{\rho|\rho\geq 0,\ \sqrt{\rho}\epsilon H_0^1(0,\infty)\}\\ W &= \{\underline{\rho}|\underline{\rho}\geq 0,\ \sqrt{\underline{\rho}}\epsilon\bigoplus_{\ell=0}^{\infty}H_0^1(0,\infty),\ \sum_{\ell=0}^{\infty}\ell(\ell+1)\int_0^\infty\frac{\rho_\ell(r)}{r^2}dr<\infty\}. \end{aligned}$$

We now show that adding the gradient term changes the ground state energy only by *const* Z^2 at most. From Hardy's inequality [10] follows

$$(3.4)\qquad \int_0^\infty \sqrt{\rho}'^2 dr \geq \int_0^\infty \frac{\rho}{4r^2} dr.$$

With this result we easily find a lower bound of the infimum of $\tilde{\mathcal{E}}_Z^{HW}$.

$$(3.5)\qquad \tilde{E}_Z^{HW}(N) = \inf\{\tilde{\mathcal{E}}_Z^{HW}(\underline{\rho}) | \underline{\rho} \epsilon W\} \geq \tilde{E}_Z^H(N),$$

since $\ell(\ell+1) + \frac{1}{4} = (\ell + \frac{1}{2})^2$ and $W \subseteq M$. This is

THEOREM 2.

$$\tilde{E}_Z^{HW}(N) \geq \tilde{E}_Z^H(N).$$

Now we state

THEOREM 3.

$$\tilde{E}_Z^{HW}(N) \leq \tilde{E}_Z^H(N) + Z^2 O(1).$$

In order to prove theorem 3 we firstly choose appropriate trial functions, secondly we prove some of their properties.

In the case of missing gradient term we found the minimizing functions in (2.7) (together with (2.8), (2.12) and (2.15)) to be ($Z=1$)

$$(3.6)\qquad \rho_\ell = \frac{q(2\ell+1)}{\pi r} \sqrt{\left[-(\ell+\frac{1}{2})^2 + r - \frac{r^2}{(2k+1)^2}\right]_+}, \quad \ell < k.$$

ϱ_ℓ is supported in the interval $[r_1', r_2']$, where

$$(3.7)\qquad r_{1,2}' = \frac{(2k+1)^2}{2}\left(1 \mp \sqrt{1 - \left(\frac{2\ell+1}{2k+1}\right)^2}\right).$$

Since for the functions in (3.6) the gradient therm has nonintegrable singularities at r_1' and r_2', we have to look for better trial functions. We divide the radial axis into three parts. In the inner and outer region we choose the trial functions similar to the wave-functions of the hydrogen atom. In the middle region we choose them according to (3.6) but with a decreased norm. Therefore we introduce the

NOTATIONS.

$$(3.8)\qquad \begin{aligned} r_{1,2} &= \frac{(2k-1)^2}{2}\left(1 \mp \sqrt{1 - \left(\frac{2\ell+1}{2k-1}\right)^2}\right), \\ R(r) &= -(\ell+\frac{1}{2})^2 + r - \frac{r^2}{(2k-1)^2}. \end{aligned}$$

Now we choose the following trial functions:

DEFINITION. For $1 \leq \ell < k-2$ let

$$\rho_\ell(r) = q(2\ell+1) \begin{cases} \alpha^2 r^{2\ell+2} & \text{for } 0 \leq r \leq x_1 \\ \frac{1}{\pi r}\sqrt{-(\ell+\frac{1}{2})^2 + r - \frac{r^2}{(2k-1)^2}} & \text{for } x_1 \leq r \leq x_2 \\ \beta^2 e^{-2\gamma r} & \text{for } x_2 \leq r \end{cases} \tag{3.9}$$

with

$$\begin{aligned} \alpha^2 &= \frac{\sqrt{R(x_1)}}{\pi x_1^{2\ell+3}}, \\ \beta^2 &= \frac{\sqrt{R(x_2)}}{\pi x_2} e^{2\gamma x_2}, \\ \gamma &= \frac{1}{\ell}, \\ x_1 &= r_1 + \ell, \\ x_2 &= r_2 - k. \end{aligned} \tag{3.10}$$

For $\ell = 0$ and $\ell \geq k-2$ we choose ϱ_ℓ to be identically zero. k is defined by (2.15).

The conditions for α and β in (3.10) assure the continuity of ϱ_ℓ.

We now show some properties of $x_1, x_2, R(x_1)$ and $R(x_2)$. Let x_m denote the maximum of $R(r)$, namely $x_m = \frac{(2k-1)^2}{2}$.

PROPOSITION 1.

$$\begin{aligned} &i) && \ell^2 \leq r_1, \qquad r_2 \leq 2x_m, \\ &ii) && x_1 \leq x_m \leq x_2, \\ &iii) && \frac{\sqrt{\ell}}{4} \leq R(x_1) \leq \ell, \\ &iv) && \frac{\sqrt{k}}{2} \leq R(x_2) \leq 2k \text{ for } k \geq 2. \end{aligned}$$

Proof: The first part of i) is proved by expansion of the square root. We obtain

$$\begin{aligned} r_1 &= \frac{(2k-1)^2}{2}\left(1 - \sum_{j=0}^{\infty} a_j \left(\frac{2\ell+1}{2k-1}\right)^{2j}\right) \geq \\ &\geq \frac{(2k-1)^2}{2}\left(1 - \left(1 - \frac{1}{2}\left(\frac{2\ell+1}{2k-1}\right)^2\right)\right) = \frac{(2\ell+1)^2}{4} \geq \ell^2, \end{aligned} \tag{3.11}$$

since $\alpha_0 = 1$, $\alpha_1 = -\frac{1}{2}$ and $\alpha_j < 0$ for $j \geq 2$.

The inequality $r_2 \leq 2x_m$ follows immediately from $\sqrt{1-(\frac{2l+1}{2k-1})^2} \leq 1$.

Since $1 < k-\ell-1$, we find

$$\ell^2 \leq k^2 \leq k^2 k \cdot 1 \leq (2k-1)^2(k+\ell)(k-\ell-1) = x_m^2 \left(1 - \left(\frac{2\ell+1}{2k-1}\right)^2\right), \tag{3.12}$$

which implies ii).

To show iii) we write

$$\begin{aligned} \ell &\geq \ell - \frac{2r_1\ell+\ell^2}{(2k-1)^2} = R(x_1) = \ell\left(1-\frac{2r_1+\ell}{2x_m}\right) \geq \ell\left(1-\frac{r_1+x_m}{2x_m}\right) \geq \\ &\geq \frac{\ell}{2}\sqrt{1-\left(\frac{2\ell+1}{2k-1}\right)^2} \geq \frac{\ell}{2\ell+3}\sqrt{2\ell+2} \geq \frac{\sqrt{\ell}}{4}. \end{aligned} \tag{3.13}$$

Analogously iv) is shown by the fact ($k \geq 2$)

$$\begin{aligned} 2k &\geq 2k\frac{r_2}{2x_m} \geq \frac{2r_2k-k^2}{2x_m} - k = R(x_2) = k\frac{2r_2-k-2x_m}{2x_m} \gtrsim \\ &\geq k\frac{r_2-x_m}{2x_m} \geq \frac{k}{2}\sqrt{1-\left(\frac{2k-3}{2k-1}\right)^2} = \frac{k}{2k-1}\sqrt{2k-2} \gtrsim \frac{\sqrt{k}}{2}. \blacksquare \end{aligned} \tag{3.14}$$

PROPOSITION 2.

$$\sum_{\ell=1}^{k'-2}\int_0^\infty \rho_\ell dr \leq N,$$

where k' denotes the greatest integer less than k.

Proof: We have

$$\begin{aligned} \int_0^\infty \rho_\ell dr &= q(2\ell+1)\left(\alpha^2\frac{x_1^{2\ell+3}}{2\ell+3} + \int_{x_1}^{x_2}\frac{\sqrt{R(r)}}{\pi r}dr + \beta^2\frac{e^{-2\gamma x_2}}{2\gamma}\right) \leq \\ &\leq q(2\ell+1)\left(\frac{\sqrt{\ell}}{\pi(2\ell+3)} + \int_{r_1}^{r_2}\frac{\sqrt{R(r)}}{\pi r}dr + \ell\frac{\sqrt{2k}}{2\pi x_2}\right) \end{aligned} \tag{3.15}$$

using (3.10) and proposition 1. The integral is just equal to $k-\ell-1$, while the sum of the other two terms is less than one, since $1 \leq \ell < k-2$ and $x_2 \geq x_m \gtrsim \frac{k^2}{2}$. Therefore, using (2.14),

$$\sum_{\ell=1}^{k'-2}\int_0^\infty \rho_\ell dr \leq \sum_{\ell=1}^{k'-2}(k-\ell)q(2\ell+1) \leq \sum_{\ell=0}^{k'}(k-\ell)q(2\ell+1) \approx N. \blacksquare \tag{3.16}$$

PROPOSITION 3.

$$\text{(i)} \qquad \sum_{\ell=1}^{k'-2} \int_0^{x_1} \left(\sqrt{\rho_\ell}'^2 + \frac{1}{3}\frac{\pi^2}{q^2(2\ell+1)^2}\rho_\ell^3 + \left(\frac{(\ell+\frac{1}{2})^2}{r^2} - \frac{1}{r} \right) \rho_\ell \right) dr \le O(1),$$

$$\text{(ii)} \qquad \sum_{\ell=1}^{k'-2} \int_{x_2}^{\infty} \left(\sqrt{\rho_\ell}'^2 + \frac{1}{3}\frac{\pi^2}{q^2(2\ell+1)^2}\rho_\ell^3 + \left(\frac{(\ell+\frac{1}{2})^2}{r^2} - \frac{1}{r} \right) \rho_\ell \right) dr \le O(k^{-1/2})$$

Proof: (i) is proved by inserting $q(2\ell+1)\alpha^2 r^{2\ell+2}$ for ϱ_ℓ:

$$q(2\ell+1) \int_0^{x_1} \left(\alpha^2(\ell+1)^2 r^{2\ell} + \frac{\pi^2}{3}\alpha^6 r^{6\ell+6} + \left(\frac{\left(\ell+\frac{1}{2}\right)^2}{r^2} - \right.\right.$$

$$\left.\left. - \frac{1}{r} \right) \alpha^2 r^{2\ell+2} \right) dr \le q(2\ell+1) \left((\ell+1)^2 \frac{\sqrt{R(x_1)}}{\pi x_1^2(2\ell+1)} + \frac{\pi^2}{3}\frac{\sqrt{R^3(x_1)}}{\pi^3 x_1^2 (6\ell+7)} + \right. \tag{3.17}$$

$$\left. + (\ell+\frac{1}{2})^2 \frac{\sqrt{R(x_1)}}{\pi x_1^2(2\ell+1)} \right) \le const \quad \ell^{-3/2}.$$

Summation over ℓ yields (i), because even $\sum_{\ell=1}^{\infty} \ell^{-m}$ is finite, if $m>1$.

To prove (ii) we insert $q(2\ell+1)\beta^2 e^{-2\lambda r}$ for ϱ_ℓ. This yields

$$q(2\ell+1) \int_{x_2}^{\infty} \left(\beta^2\gamma^2 e^{-2\gamma r} + \frac{\pi^2}{3}\beta^6 e^{-6\gamma r} + (\ell+\frac{1}{2})^2 \beta^2 \frac{e^{-2\gamma r}}{r^2} - \right.$$

$$\left. - \beta^2 \frac{e^{-2\gamma r}}{r} \right) dr \le q(2\ell+1) \left(\frac{\gamma}{2}\frac{\sqrt{R(x_2)}}{\pi x_2} + \frac{\pi^2}{3}\frac{\sqrt{R^3(x_2)}}{6\pi^3 x_2^3 \gamma} + \right.$$

$$\left. + (\ell+\frac{1}{2})^2 \frac{\sqrt{R(x_2)}}{\pi x_2^2} \left(1 - 2\gamma x_2 e^{2\gamma x_2} E_1(2\gamma x_2)\right) \right) \le const \left(k^{-3/2} + \right. \tag{3.18}$$

$$\left. + k^{-5/2} + k^{-7/2}(\ell+\frac{1}{2})^3 \left(1 - \frac{2\gamma x_2}{2\gamma x_2 + 1}\right) \right) \le const(k^{-3/2} + k^{-5/2} +$$

$$+ k^{-3/2}),$$

where we used formula 5.1.19 of Abramowitz and Stegun [11] for the exponential integral function. Summation over ℓ completes the proof of (ii). ■

PROPOSITION 4.

$$\sum_{\ell=1}^{k'-2} \int_{x_1}^{x_2} \sqrt{\rho_\ell}'^2 dr \le O(1).$$

Proof: The integrand is explicitly

$$\sqrt{\rho_\ell}\,'^2(r) = \frac{q(2\ell+1)}{16\pi}\left(\frac{4\left(\ell+\frac{1}{2}\right)^4}{r^3\sqrt{R^3(r)}} - \frac{4\left(\ell+\frac{1}{2}\right)^2}{r^2\sqrt{R^3(r)}} + \frac{1}{r\sqrt{R^3(r)}}\right) \tag{3.19}$$

for $x_1 \leq r \leq x_2$. Calculating the integral in proposition 4 one finds

$$\begin{aligned}\int_{x_1}^{x_2} \sqrt{\rho_\ell}\,'^2 dr = \frac{q(2\ell+1)}{16\pi} &\left[\frac{3(\frac{2\ell+1}{2k-1})^2 - 5}{2\left(\ell+\frac{1}{2}\right)^3} \arcsin \frac{r - 2\left(\ell+\frac{1}{2}\right)^2}{r\sqrt{1-(\frac{2\ell+1}{2k-1})^2}} + \right. \\ &+ \frac{5r}{(2k-1)^2\left(\ell+\frac{1}{2}\right)^2\sqrt{R(r)}} - \frac{5}{\left(\ell+\frac{1}{2}\right)^2\sqrt{R(r)}} + \frac{6}{(2k-1)^2\sqrt{R(r)}} + \\ &\left. + \frac{1}{r\sqrt{R(r)}} + \frac{2\left(\ell+\frac{1}{2}\right)^2}{r^2\sqrt{R(r)}}\right]_{x_1}^{x_2}.\end{aligned} \tag{3.20}$$

Since the coefficient of the arcsin term is negative and arcsin as well as its argument are strictly increasing functions, we can omit this term. We estimate the other negative terms also by zero. Using proposition 1 we get

$$\begin{aligned}\int_{x_1}^{x_2} \sqrt{\rho_\ell}\,'^2 dr \leq q(2\ell+1) &\left\{\frac{5x_2}{(2k-1)^2\left(\ell+\frac{1}{2}\right)^2\sqrt{R(x_2)}} + \right. \\ &\left. + \frac{5}{\left(\ell+\frac{1}{2}\right)^2\sqrt{R(x_1)}} + \frac{6}{(2k-1)^2\sqrt{R(x_2)}} + \frac{1}{x_2\sqrt{R(x_2)}} + \frac{2\left(\ell+\frac{1}{2}\right)^2}{x_2^2\sqrt{R(x_2)}}\right\} \leq \\ &\leq const\left(\frac{1}{\ell k^{1/4}} + \frac{1}{\ell^{5/4}} + \frac{\ell}{k^{9/4}} + \frac{\ell^3}{k^{17/4}}\right) \leq const\,\ell^{-5/4}.\end{aligned} \tag{3.21}$$

Summation over ℓ yields the desired result as in the proof of proposition 3 (i). ■

PROPOSITION 5.

$$\begin{aligned}&\sum_{\ell=1}^{k'-2}\int_{x_1}^{x_2}\left(\frac{\pi^2}{3q^2(2\ell+1)^2}\rho_\ell^3 + \left(\frac{\left(\ell+\frac{1}{2}\right)^2}{r^2} - \frac{1}{r}\right)\rho_\ell\right) dr \leq \\ &\leq \sum_\ell q(2\ell+1)\int_{r_1}^{r_2}\left(\frac{\pi^2}{3}\left(\frac{\sqrt{R(r)}}{\pi r}\right)^3 + \left(\frac{\left(\ell+\frac{1}{2}\right)^2}{r^2} - \frac{1}{r}\right)\frac{\sqrt{R(r)}}{\pi r}\right) dr + \\ &+ O(1).\end{aligned}$$

Proof: Since the ρ_ℓ^3 and the centrifugal term are positive, we need only consider the potential term.

$$\int_{x_1}^{x_2} \frac{-\rho_\ell}{r} dr = q(2\ell+1) \int_{x_1}^{x_2} \frac{-\sqrt{R(r)}}{\pi r^2} dr = q(2\ell+1) \left(\int_{r_1}^{r_2} \frac{-\sqrt{R(r)}}{\pi r^2} dr + \right.$$

$$(3.22) \quad + \int_{r_1}^{x_1} \frac{\sqrt{R(r)}}{\pi r^2} dr + \left. \int_{x_2}^{r_2} \frac{\sqrt{R(r)}}{\pi r^2} dr \right) \le q(2\ell+1) \left(\int_{r_1}^{r_2} \frac{-\sqrt{R(r)}}{\pi r^2} dr + \right.$$

$$\left. + \frac{\sqrt{R(x_1)}}{\pi r_1^2}(x_1 - r_1) + \frac{\sqrt{R(x_2)}}{\pi x_2^2}(r_2 - x_2) \right) \le q(2\ell+1) \left(\int_{r_1}^{r_2} \frac{-\sqrt{R(r)}}{\pi r^2} dr + \right.$$

$$\left. + const(\ell^{-5/2} + k^{-5/2}) \right),$$

where we used the fact that $\sqrt{R(r)}$ is monotone increasing between r_1 and x_1 and monotone decreasing between x_2 and r_2. Summation over ℓ completes the proof. ■

Now we are ready to prove theorem 3.

Proof of the theorem 3: First we remark that the functional $\tilde{\mathcal{E}}_Z^{HW}$ and so its minimum is enlarged by substituting $\ell(\ell+1)$ by $\left(\ell+\frac{1}{2}\right)^2$. We showed earlier [8] that $\tilde{\mathcal{E}}_Z^{HW} = Z^2 \tilde{\mathcal{E}}_1^{HW}$ holds and that we may use the condition $\sum_\ell \int \rho_\ell dr \le N$ rather than $\sum_\ell \int \rho_\ell dr = N$. Therefore we have

$$(3.23) \quad \tilde{E}_Z^{HW}(N) \le Z^2 \sum_\ell \mathcal{E}_{\ell,1}^{HW}(\rho_\ell)$$

for every set of admissible functions ϱ_ℓ. We take the functions defined in (3.9). We showed in the above propositions that $(\rho_0, \ldots, \rho_\ell, \ldots) \epsilon W$ and $\sum_\ell \int_0^\infty \rho_\ell dr \le N$, hence our set of trial functions is admissible. Thus using propositions 3,4 and 5 we get

$$(3.24) \quad \begin{aligned} \tilde{E}_Z^{HW}(N) \le Z^2 & \left(\sum_{\ell=1}^{k'-2} \int_{r_1}^{r_2} q(2\ell+1) \left(\frac{\pi^2}{3} \frac{\sqrt{R^3(r)}}{(\pi r)^3} + \right.\right. \\ & \left.\left. + \left(\frac{\left(\ell+\frac{1}{2}\right)^2}{r^2} - \frac{1}{r} \right) \frac{\sqrt{R(r)}}{\pi r} \right) dr + O(1) \right). \end{aligned}$$

The integral, however, is just $E_{\ell,1}^H \left(q(2\ell+1)(k-1-\ell)\right) = -q\frac{k-1-\ell}{2k-1}$, where we used (2.9). This yields

$$\tilde{E}_Z^{HW}(N) \le -\frac{Z^2 q}{2k-1} \sum_{\ell=1}^{k'-2} (k-1-l) + Z^2 O(1) =$$

$$(3.25) \quad = -\frac{Z^2 q}{2k-1} \left((k'-2)(k-1) - \frac{1}{2}(k'-2)(k'-1) \right) =$$

$$= -\frac{Z^2 q}{4}(k + O(1)) = \tilde{E}_Z^H(N) + Z^2 O(1)$$

because of (2.15) and theorem 1. ■

In the case where $N/Z = \lambda$ is fixed the analogue holds for Thomas-Fermi-Weizsäcker theory (Lieb [12]). The gradient term changes the energy by *const* Z^2 in this case, too. Finally we remark that omitting the $\ell = 0$ term as well as omitting the outermost shell (we wrote $k-1$ instead of k) results in changes of order $Z^2O(1)$ in the energy.

4. An Upper Bound for the Quantum Mechanical Energy

We are now able to draw our final conclusion.

THEOREM 4. *In the noninteracting case*

$$E_Q(Z,N) \leq \tilde{E}_Z^H(N) + Z^2O(1) = -\frac{q}{4}\left(\frac{3}{q}\right)^{1/3} Z^2N^{1/3} + Z^2O(1).$$

Proof: As in [8] we can prove that for every $\underline{\rho}\epsilon W$ with $\sum_{\ell=0}^{\infty}\int_0^{\infty}\rho_\ell dr \leq N$

$$\begin{aligned} E_Q(Z,N) &\leq \tilde{\mathcal{E}}_Z^{HW}(\rho_0,\dots,\rho_\ell,\dots) + \\ &+ \sum_{\substack{\ell=0\\ N_\ell\neq 0}}^{\infty} \frac{\alpha_\ell}{3}\left(\frac{-1+6\varepsilon_\ell-3\varepsilon_\ell^2}{N_{\ell,m,s}^2} + \frac{2\varepsilon_\ell^3-6\varepsilon_\ell^2+4\varepsilon_\ell}{N_{\ell,m,s}^3}\right)\int_0^\infty \rho_\ell^3 dr \end{aligned} \tag{4.1}$$

where $N_{\ell,m,s}$ is an abbreviation for $\int_0^\infty \frac{\rho_\ell}{q(2\ell+1)}dr$ and ε_ℓ is the difference between $N_{\ell,m,s}$ and the greatest integer less than or equal to $N_{\ell,m,s}$. For $\underline{\rho}$ we choose the functions defined in (3.9) and (3.10). These functions satisfy the above mentioned conditions. In the previous chapter we estimated the value of the Hellmann-Weizsäcker functional for these trial functions. Thus we have

$$\begin{aligned} E_Q(Z,N) \leq Z^2 \Bigg\{ &\tilde{E}_1^H(N) + O(1) + \sum_{\ell=1}^{k'-2}\frac{\alpha_\ell}{3}\left(\frac{-1+6\varepsilon_\ell-3\varepsilon_\ell^2}{N_{\ell,m,s}^2} + \right. \\ &\left. + \frac{2\varepsilon_\ell^3-6\varepsilon_\ell^2+4\varepsilon_\ell}{N_{\ell,m,s}^3}\right)\int_0^\infty \rho_\ell^3 dr\Bigg\}. \end{aligned} \tag{4.2}$$

We need estimates for $\int_0^\infty \rho_\ell^3 dr$ and $N_{\ell,m,s}$.

$$\begin{aligned} \int_0^\infty \rho_\ell^3 dr &= q^3(2\ell+1)^3\left(\frac{\sqrt{R^3(x_1)}}{\pi^3x_1^2(6\ell+7)} + \int_{x_1}^{x_2}\frac{\sqrt{R^3(r)}}{\pi^3r^3}dr + \frac{\sqrt{R^3(x_2)}}{6\pi^3x_2^3\gamma}\right) \leq \\ &\leq const\; q^3(2\ell+1)^3\left(\ell^{-7/2} + \frac{3}{\pi^2}\frac{(k-1-\ell)^2}{(2\ell+1)(2k-1)^2} + k^{-7/2}\right). \end{aligned} \tag{4.3}$$

For $N_{\ell,m,s}$ we find

$$N_{\ell,m,s} \geq k - \ell - \frac{3}{2} \geq \frac{1}{2} \tag{4.4}$$

in the following way:

$$N_{\ell,m,s} \geq \int_{x_1}^{x_2} \frac{\sqrt{R(r)}}{\pi r} dr =$$

$$= \frac{1}{\pi}\Big\{\sqrt{R(x_2)} - \sqrt{R(x_1)} - (\ell + \frac{1}{2})(\arcsin(1 - s_1) + \arcsin(1 - s_2)) +$$

$$+ \frac{2k-1}{2}(\arcsin(1 - t_1) + \arcsin(1 - t_2))\Big\}$$

with $0 < s_i = 1 \pm \frac{x_i - 2(\ell+\frac{1}{2})^2}{x_i \delta}$, $0 < t_i = 1 \pm \frac{2x_i - (2k-1)^2}{(2k-1)^2 \delta} \leq 1$, and $\delta = \sqrt{1 - \frac{(2\ell+1)^2}{(2k-1)^2}}$. The upper sign refers to $i = 1$ whereas the lower sign refers to $i = 2$. Using 4.4.41 of Abramowitz and Stegun [11] we obtain

$$\arcsin\,(1 - x) \leq \frac{\pi}{2} - \sqrt{2x}(1 + a_1 x) \text{ for } 0 \leq x \leq 2,$$

$$\arcsin\,(1 - x) \geq \frac{\pi}{2} - \sqrt{2x}(1 + a_1 x + dx^2) \text{ for } 0 \leq x \leq 1$$

where α_1 and d are certain constants. Using the estimates

$$\frac{\sqrt{8k-8}}{2k-1} \leq \delta \leq 1 - \frac{1}{2}\frac{(2\ell+1)^2}{(2k-1)^2},$$

$$\frac{2\ell+1}{2k-1}\sqrt{\frac{s_1}{t_1}} \geq 1 + \delta - \frac{1+\delta}{1-\delta}\frac{2\ell}{(2k-1)^2},$$

$$\sqrt{\frac{s_1}{t_1}}^3 \geq \frac{(2\ell+1)^3}{(2k-1)^3},$$

$$\sqrt{\frac{s_2}{t_2}} \geq \frac{2\ell+1}{2k-1}\frac{1}{1+\delta},$$

$$\sqrt{\frac{s_2}{t_2}}^3 \geq \frac{(2\ell+1)^3}{(2k-1)^3}(1 - 4\delta),$$

$$\sqrt{R(x_1)} \leq \sqrt{\ell\delta},$$

$$\sqrt{R(x_2)} \geq \sqrt{k\delta}\left(1 - \frac{k}{(2k-1)^2\delta}\right)$$

yields the result of (4.4).

Because of (4.3) and (4.4) the inequality (4.2) reads now

$$E_Q(Z,N) \leq Z^2 \left\{\tilde{E}_1^H(N) + O(1) + \sum_{\ell=1}^{k'-2} const \frac{q(2\ell+1)}{(k-\ell-\frac{3}{2})^2}\left(\ell^{-7/2} + \right.\right.$$

$$\left.\left. + \frac{(k-1-\ell)^2}{(2\ell+1)(2k-1)^2} + k^{-7/2}\right)\right\} \leq Z^2\left(\tilde{E}_1^H(N) + O(1) + \right. \tag{4.5}$$

$$+ \sum_{\ell=1}^{k'-2} const \frac{1}{\ell^2(k-\frac{3}{2}-\ell)^2} + O(k^{-1}) + O(k^{-3/2}) \Bigg).$$

The sum in (4.5) may be bounded by an inequality of McLaurin and Cauchy (Hardy, Littlewood and Polya [10]: theorem 154) which states

$$\frac{1}{n}\sum_{\ell=1}^{n-1} f\left(\frac{\ell}{n}\right) \leq \int_0^1 f(x)dx,$$

if f is nonnegative, decreasing for $0 \leq x \leq \xi \leq 1$ and increasing for $0 \leq \xi \leq x \leq 1$. In our case we choose

$$f(x) = \begin{cases} \frac{n}{(x_0-1)^2}, & \text{for } 0 \leq x \leq \frac{1}{n} \\ \frac{1}{nx^2(x_0-nx)^2}, & \text{for } \frac{1}{n} \leq x \leq \frac{n-1}{n} \\ \frac{n}{(n-1)^2(x_0-n+1)^2}, & \text{for } \frac{n-1}{n} \leq x \leq 1 \end{cases}$$

where $n = k' - 1$ and $x_0 = k - \frac{3}{2}$. Evaluating the integral one finds that the sum in (4.5) is at most of order k^{-2}. Hence the additional term in (4.1) is at most of order $Z^2N^{-1/3}$. This proves the theorem. ■

Scott [6] already remarked, that the Z^2-correction should be independent of the interaction of the electrons because this correction stems from the innermost electrons, where the field is sufficiently close to a Coulomb potential. Therefore we hope to be able to generalize our result to the case, where interaction is taken into account [9]. This would be the first part of a proof of Scott's conjecture: The leading correction is bounded from above by a term of order Z^2. The next step would be to calculate the coefficient of the Z^2-term and to find a corresponding lower bound.

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